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DERIVATIZATION OF ACIDIC ORGANIC COMPOUNDS USING PHASE TRANSFER CATALYSIS

V.Y. Taguchi and O.W. Berg

Ontario Ministry of the Environment, Rexdale, Ontario M9W 5L1

Derivatization procedures are usually incorporated into the analyses of acidic organic compounds such as phenols and carboxylic acids in order to improve their chromatographic properties. Classical organic chemistry is the basis for some common derivatizing agents. Diazomethane has been used to derivatize phenols and carboxylic acids to their corresponding anisoles and methyl esters respectively. Acetic anhydride has been used to acetylate phenols, alcohols and amines. Acetylation relies on the nucleophilicity of the phenol and the electrophilicity of the acetylating agent. Some phenols such as 2,4-dinitrophenol and 4,6-dinitro-o-cresol are difficult to derivatize with acetic anhydride. This may be due to delocalization of electron density from the phenolic oxygen into the nitro groups via resonance stabilization. The net result may be a poor nucleophile.

Phase transfer catalysis or extractive alkylation was applied to phenolic compounds by Rosenfeld and Taguchi [1]. The phase transfer agent used was tetrahexylammonium hydroxide (THAH). The following scheme illustrates this technique.



The phenol (ArOH) is ionized in an alkaline solution (step 1). The phenol anion forms an ion pair with a tetraalkylammonium cation (THA⁺) (step 2). This ion pair is soluble in both the aqueous and the organic phases and is partitioned between them (step 3). If the organic phase contains an alkylating agent such as methyl iodide, irreversible alkylation occurs in this phase (step 4). This shifts the equilibrium towards the alkylated derivative. This process relies on formation an ion pair of the analyte with the phase transfer agent. The speed of derivative formation and the yield of the derivative are dependent on the efficiency of the extraction and the rate of reaction of the ion pair with the alkylating agent. The efficiency of extraction of the anion of the analyte is determined by the properties and concentrations of the ions of the ion pair, the lipophilicity of the ion pair and the properties of the solvent. The most frequently used phase transfer agents are the tetrabutyl-, tetrapentyl- and tetrahexylammonium hydroxides. In general, the pH of the aqueous phase should be at least 2 units higher than the pKa value of the acidic analyte. The organic solvents are

generally aprotic such as dichloromethane or toluene although some alcohols have been used.

Phase transfer catalysis has been applied to a series of substituted phenols (alkylated, chlorinated and nitrated). Initial experiments have shown that methylation to the corresponding anisoles occurs within 1 hour at room temperature for most of the phenols studied. No product was obtained with 4,6-dinitro-o-cresol. This may be due to lack of formation of the ion pair because of steric hindrance. This may be a limiting factor in the applicability of the technique.

One of the problems associated with phase transfer catalysis is elimination of the excess and reacted ion pair agent. This was accomplished using a short column of Florisil. The anisole derivatives were eluted with dichloromethane while the ion pair agent remained on the column. When an insufficient amount of Florisil was used, excess reagent was isolated with the products. In a GC-MS equipped with an on-column injector, the excess THAH underwent a Hoffmann degradation to form trihexylamine which appeared as a broad peak in the chromatogram.

Further experiments are underway to optimize conditions for environmentally significant phenols.

1. J.M. Rosenfeld and V.Y. Taguchi, Anal. Chem., 48, 726 (1976).

